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# INCREASES OF NITRATE IN THE GREAT LAKES

**by**

**J. Barica**

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National Water Research Institute
Lakes Research Branch
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

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Environment Canada

**AUGMENTATIONS DU NITRATE DANS LES GRANS LACS**

J. BARICA

Direction de la recherche sur les lacs
Institut national de recherche sur les eaux
Burlington, Ontario
Canada

RÉSUMÉ

Dans les Grands Lacs laurentiens, les plus grandes étendues d'eau douce au monde, les cncentrations de nitrate ont augmenté de 200 % et plus au cours des vingt dernières années. Dans le cas du lac Supérieur, on a noté une augmentation d'un facteur quatre au cours des soixante dernières années et d'un facteur six au cours des trente dernières anées à Hamilton Harbour, lac Ontario. Les concentrations absolues sont demeurées faibles (200-400 ugN/L) et ne constituent pas une menace directe pour la qualité de l'eau potable. Elles peuvent cependant avoir d'importantes répercussions sur la gestion du phosphore dans le bassin des Grands Lacs en augmentant les rapports N:P qui régissent la composition des espèces de phytoplancton.

On y présente une analyse préliminaire des causes et des effets possibles de la nitrification des Grands Lacs. On conclut que les augmentations des concentrations de nitrate dans les Grands Lacs sont le résultat de plusieurs facteurs d'importance relative différente. Dans le bassin inférieur des Grands Lacs, l'augmentation de la population, l'utilisation accrue d'engrais en agriculture et la diminution importante des concentrations de phosphore sont des facteurs importants. Dans le bassin supérieur des Grands Lacs (Huron et Supérieur), le facteur le plus important est le dépôt atmosphérique de nitrate dans les pluies acides.

**PERSPECTIVE GESTION**

La présent document a été rédigé afin d'être présenté et publié lors du 5e Colloque international du CSIF (Centre scientifique international des fertilisants) dont le thème est : "Protection de la qualité de l'eau contre les émissions nocives, avec une attention spéciale au nitrate" qui doit se tenir à Balatonfured, Hongrie, en septembre 1987.

La concentration de nitrate dans les Grands Lacs a augmenté au cours des vingt dernières années de 30 à 200 % et plus. Dans le cas du lac Supérieur, on a noté une augmentation d'un facteur quatre au cours des soixante dernières années, et d'un facteur six au cours des trente dernières années à Hamilton Harbour, lac Ontario. Bien que les concentrations absolues soient encore faibles (200-400 ug/L) et ne constituent pas une menace directe pour la qualité de l'eau potable, elles peuvent avoir des répercussions sur la gestion du phosphore en augmentant les rapports N:P, qui régissent la composition des espèces de phytoplancton.

Ce document présente une analyse préliminaire des causes et des impacts possibles de la nitrification des Grands Lacs. On suppose que l'augmentation des concentrations de nitrate dans les Grands Lacs est le résultat combiné de plusieurs facteurs d'importance relative différente : l'augmentation de la poulation, l'utilisation accure d'engrais en agriculture, la diminution des concentrations de phosphore dans les eaux usées municipales et les précipitations atmosphériques (oxydes d'azote dans les pluies acides). L'analyse quantitative de ces facteurs est en cours et le rapport final devrait être prêt en 1988-1989.

# INCREASES OF NITRATE IN THE GREAT LAKES

J. BARICA
Lakes Research Branch
National Water Research Institute
Burlington, Ontario
Canada

ABSTRACT

In the Laurentian Great Lakes, the world's largest freshwater system, the concentrations of nitrate have increased over the past twenty years by 200 % and over.In Lake Superior, this increase has been four-fold in sixty years, and in Hamilton Harbour on Lake Ontario, six-fold in thirty years. The absolute concentrations remain low (200 - 400 ugN/L) and do not pose a direct threat to drinking water quality.They may,however, have a significant implication on phosphorus management in the Great Lakes basin by raising N : P ratios, which are known to govern phytoplankton species composition

A preliminary analysis of possible causes and impacts of nitrifying the Great Lakes is presented. It is concluded that the increases of nitrate in the Great Lakes are a combined result of several factors of differing relative importance. In the lower Great Lakes, the increased human population, increased use of fertilizers in agriculture and large-scale phosphorus reductions are predominant. In the upper Great Lakes (Huron, Superior), atmospheric deposition of nitrate in acid rain is most significant.

Increases of nitrate in the Great Lakes,by J.Barica.

Management perspective.

This report was prepared for presentation and publication at the 5th International Symposium of CIEC (International Scientific Centre of Fertilizers),with the theme "Protection of Water Quality from harmful emmissions with special reference to Nitrate",to be held in Balatonfured,Hungary,in September 1987.

The concentration of nitrate in the Great Lakes have increased over the past twenty years by 30 - 200% and more.In Lake Superior,this increase has been fourfold in sixty years,and in Hamilton Harbour in Lake Ontario,sixfold in thirty years.While the absolute concentrations remain still low (200 -400 ug/L) and do not pose a direct threat to drinking water quality,they may have an implication on phosphorus management by raising N:P ratios,which are known to govern phytoplankton species composition.

The paper presents a preliminary analysis of possible causes and impacts of nitrifying the Great Lakes.It was suggested that the increases of nitrate in the Great Lakes are a combined result of several factors which may assume different relative importance. These factors are increasing human population,increased use of fertilizers in agriculture,phosphorus reductions in municipal waste water and atmospheric precipitation (nitrogen oxides in acid rain). The quantitative analysis of these factors is in progress and scheduled for final report in 1988/89.

INTRODUCTION

In 1972, the governments of Canada and the United States signed the Great Lakes Water Quality Agreement, recognizing the fact that the Laurentian Great Lakes, the largest freshwater system in the world (Fig. 1) and a vital natural renewable resource shared by both countries, were seriously deteriorated by pollution, particularly eutrophication and contamination by toxic chemicals. The coordinated activity resulted in a massive cleanup, unprecedented in history: major municipal wastewater treatment programs were implemented with expenditures totalling over eight billion dollars; industrial controls and phosphate limitations in detergents produced a reduction and in some areas even reversal of the eutrophication process. The longterm trends of total phosphorus concentrations -with phosphorus being a key element in the eutrophication process- have been downward since the mid 70's when legislation on phosphorus reduction was put into effect (Dobson, 1981, Kwiatkowski, 1984, Bird and Rapport, 1986). Nuisance algal blooms are no longer a common occurrence and Cladophora infestations of near-shore areas are declining (Painter, 1985).

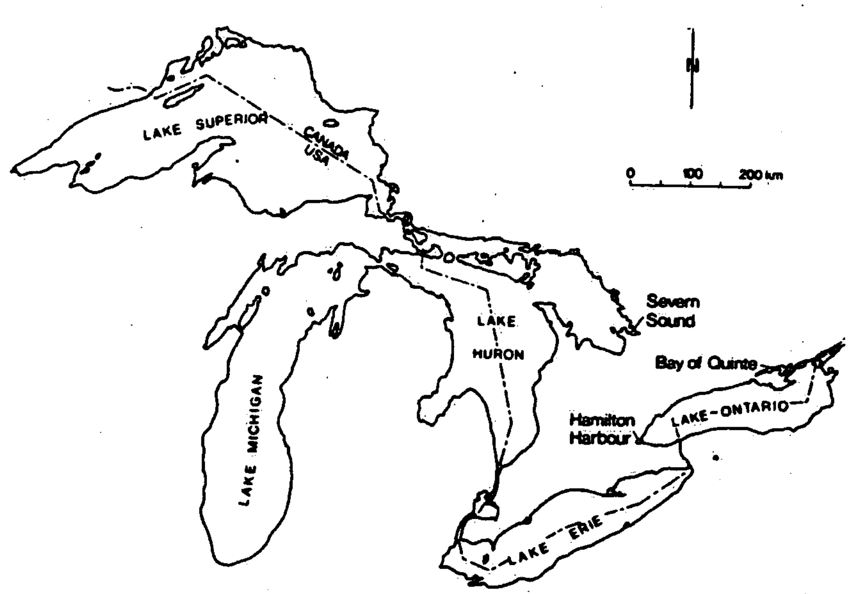


Fig. 1. The Laurentian Great Lakes.

Concurrently, with the success in phosphorus control, another phenomenon became visible: the nitrate concentrations increased alarmingly, exceeding levels of the 60's several fold. It was soon realized that other nutrients require control as well, and that unwise planning with respect to other nutrients may reduce achievements of phosphorus control. The International Joint Commission's biennial report (1986) recommended consideration of the implications of increased nitrate levels in the Great Lakes.

This report provides a preliminary analysis of the state-of-the-art of this problem, highlighting some characteristic examples, suggesting possible causes, and assessing potential water quality implications. A project to determine the extent of the problem and its implications is in progress

## LONG-TERM UPWARD TRENDS OF NITRATE AND THEIR IMPLICATIONS FOR WATER QUALITY

Dobson (1981) presented trends of springtime nitrate in Lake Superior, Lake Huron and Georgian Bay, Lake Ontario and Eastern Lake Erie, between 1960 and 1980,based on extensive data from Great Lakes water quality sueveillance programmes (Fig.2). While the concentrations were still low from the health and drinking water quality point of view (0.3-0.4 mg/l NO3-N, as compared to 10 mg/l considered to be a dangerous level for drinking water;Health & Welfare Canada,1978), the relative increases over the past twenty years were between 30 to over 200%, with highest percentage increases in the most populated and agriculturally productive basins of Lake Ontario and Lake Erie.

Bennett (1986) extended the trend analysis to include historic records back to 1906 and a focus on Lake Superior, a lake which has the largest surface area of any freshwater lake in the world and the second largest volume. Lake Superior differs from other Great Lakes: it is located mostly in the Canadian Shield region of North America, having igneous and metamorphic rocks which are strongly resistant to weathering. The basin has a 95 percent forest cover, little agricultural activity and extremely low human population density. The average flushing time is 170 years. Chemical composition of the lake water is almost unaffected by cultural development within the basin. Yet, nitrate concentration in Lake Superior increased exponentially fourfold between the years 1906 and 1973. Bennett's non-linear time series (Fig.3) include extrapolations beyond the time interval of the observations, both backward in time to 1880 and forward to the year 2000 to enable projection of the future trend.

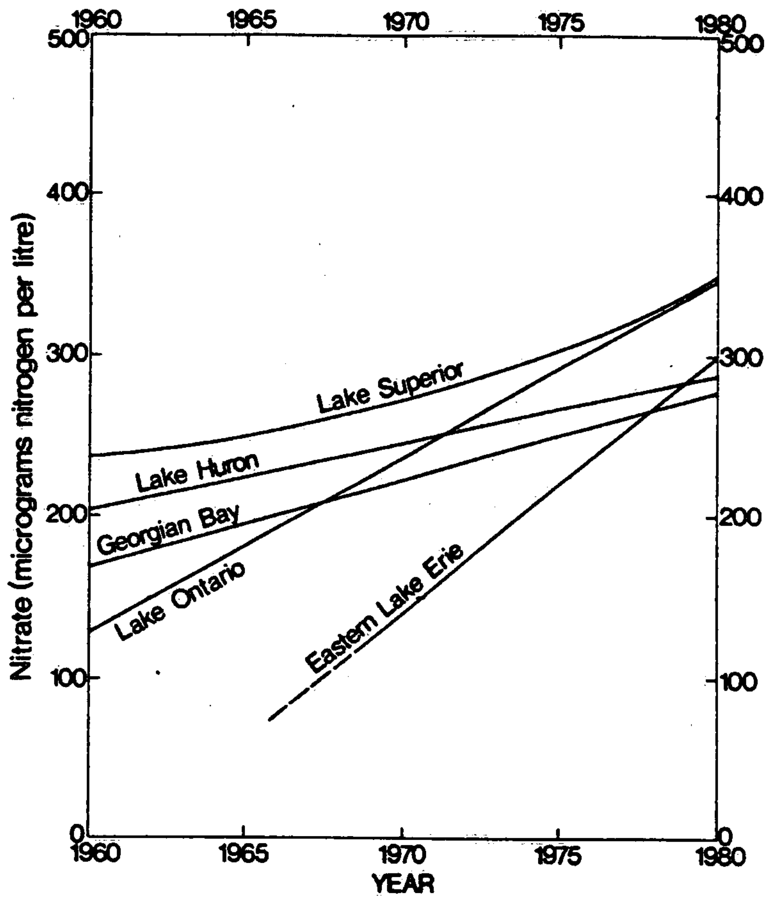


Fig. 2. Increases of springtime nitrate in the Great lakes, 1960-1980 (from Dobson, 1981)

Data presented so far were based on open lake sampling sites. The Great Lakes abound with numerous large and small near-shore embayments, with limited water exchange with the main lakes.. Hamilton Harbour is such an embayment, located at the western-most tip of Lake Ontario (8x5 km, 2.8x108 m3) in a densely populated and industrialized area ( about 0.5 million inhabitants within the 500 km2 drainage basin, with two sewage treatment plants and many industrial effluents). Here, the nitrate increases have been even more dramatic. Between 1948 and 1979, the average annual concentrations of nitrate in Hamilton Harbour increased six-fold (Forde, 1979, Fig. 4). Significant increases have been observed also in the Bay of Quinte, Lake Ontario (Robinson, 1986) and Severn Sound, in Georgian Bay on Lake Huron (MOE RAP report, 1987).

Despite these dramatic increases, the lake water itself and its quality does not seem to be directly affected by nitrate or to be in danger for the foreseeable period of time.

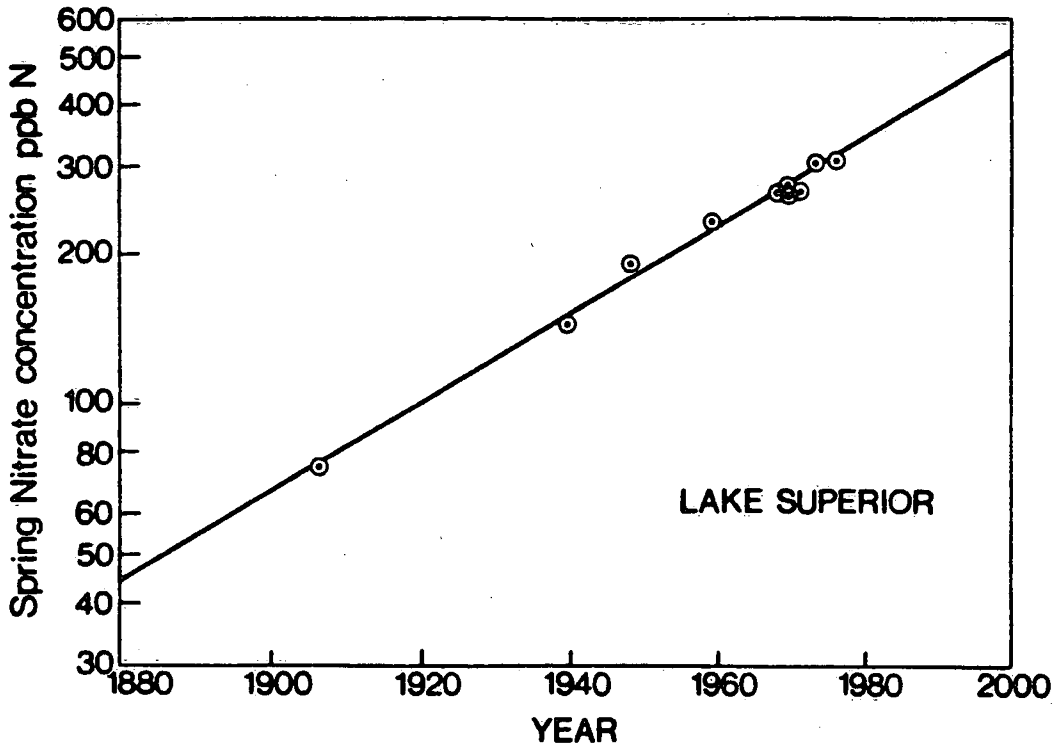


Fig. 3. Spring nitrate concentrations in Lake Superior, 1906-1976 (extrapolated 1880-2000).From Bennett, 1986.

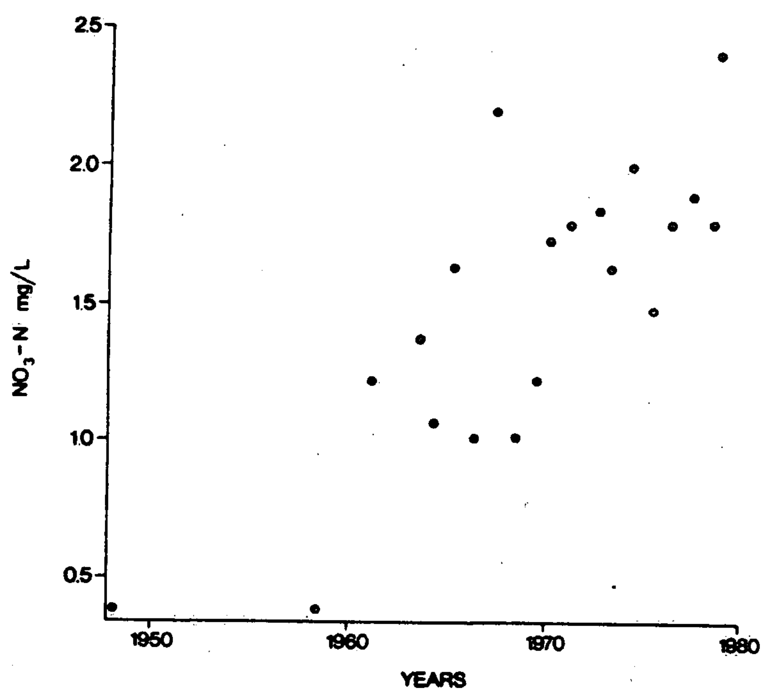


Fig. 4. Increase of nitrate in Hamilton Harbour, Lake Ontario, 1948--1979. Annual average for all stations. (After Forde, 1979)

However, the situation with regard to the sources of nitrogen is different. If we accept that the nitrate increases in lake water are exponential (Bennett, 1986), the nitrogen loading from whatever sources (see next section) must have increased exponentially also, with about the same doubling time, and at proportionally much higher and dangerous concentrations near the source, prior to dilution by lake water.

Impact on lake water quality is so far indirect, mainly through alteration of N:P ratios. These are known to govern phytoplankton succession, particularly the onset of blue-green algae and formation of algal blooms. The low values (5:1 or less, Allan and Kenney, 1980) are characteristic of hypereutrophic systems, while values over 30:1 are typical of oligotrophic lakes (Forsberg, 1979, Smith, 1983). Increases of nitrate raise total dissolved nitrogen levels and thus N:P ratios. This is even more pronounced if P values decrease concurrently during the same period. This has been the case of the Great Lakes since introduction of phosphorus control legislation in Canada and the U.S. in the early seventies. Stevens and Neilson (1987) estimated that the total phosphorus (TP) loading to Lake Ontario has declined from 14,000 t/ yr in 1969 to 8,900 t/ yr in 1982, with corresponding TP mid-lake spring concentrations decreasing from a maximum of 31 ug/L/yr in 1973 to 13 ug/L/yr in 1982. During the same period, spring nitrate (measured together with nitrite) has increased at a rate of 9.5 ug/L/yr causing N:P ratios to increase from 10 to 32 (Fig.5).

N:P ratio increases have been reported from the Bay of Quinte (up to 24.4, Robinson, 1986) and Severn Sound (threefold increases between 1969 and 1986 - up to 37.8 from 12.0; MOE RAP Report,1987). In all these cases, the increases of N:P ratios were due to a combined effect of nitrate increases and simultaneous phosphorus decreases by P control measures (upgrading of sewage treatment plants by chemical P-removal). This is a relatively beneficial phenomenon causing an "oligotrophicating" effect, and further improvement of Lake Ontario's trophic state, provided that P control measures are maintained.Relaxation of phosphorus controls would allow catastrophic eutrophication when large pool of nitrogen is already present.

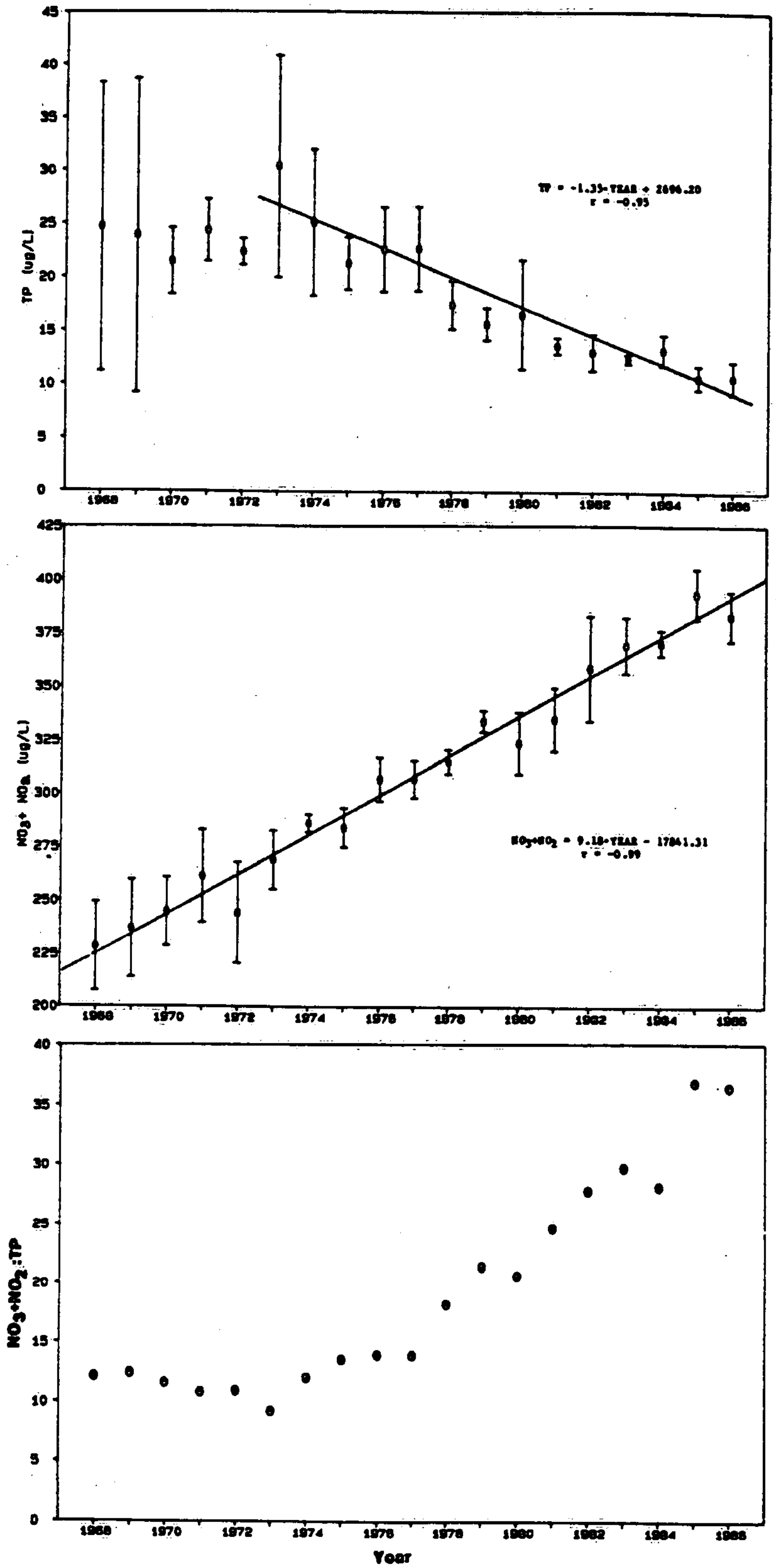


Fig. 5. Trends of spring total phosphorus concentrations, spring nitrate + nitrite and spring N:P ratios in Lake Ontario, 1969 to 1982. (After Stevens and Neilson, 1987).

CAUSES OF NITRATE INCREASES

No thorough quantitative analysis of the nitrogen sources has been attempted yet. There is however some fragmented information which makes it possible to hypothesize on possible sources of nitrates. These are: 1) phosphorus controls; 2) increased loadings from municipal and industrial sources 3) increased use of fertilizers and intensive cattle farming, and 4) long-range atmospheric transport.

1. Phosphorus controls. Underutilization of the available nitrate because of lower algal densities and demand brought about by phosphorus controls certainly leave significant "excess" nitrate and results in increasing N:P ratios: a 50% reduction of TP concentrations would double the ratio, and explain perhaps increases in N:P ratio of previously eutrophic parts of lakes which have responded to P controls. This hypothesis would not explain, however, several fold increases in Lake Superior, even before the P-control measures were implemented.

2. Nitrogen loadings from point sources. The human population explosion in the Great Lakes Basin (6.3 million in 1900, 25.5 million in 1980 excluding Lake Michigan, Dobson, 1981) caused a dramatic increase in inputs of nutrients to the Great Lakes, with nitrogen and phosphorus being the major cause of eutrophication which peaked in early seventies. The most dramatic increases of population were in the basins of Lake Erie and Ontario (from 3.1 million to 14.7 million, and 1.9 million to 7.8 million, respectively, during the past 80 years). While the P loadings to the lakes from major tributaries have been decreasing since 1972 - 75, the nitrogen loadings continued to increase, as demonstrated by Lam et al, 1983, for Lake Erie (Fig.6). Nitrate plus nitrite loads have increased there since 1967 at an average rate of 7800 metric tonnes per year.

3. Agriculture;loadings from non-point sources. There is a good correlation of increases of NO3 in the Great Lakes Basin with the extent of agriculture, particularly around Lake Ontario and Erie. Here, nitrate levels in ground water used for drinking water frequently exceed the 10 mg/l NO3-N drinking standard (Neilsen et al, 1978).

Amounts of fertilizer N used in the basin watersheds ranged from 30,000 kg (12.0 kg/watershed ha) to about 300,000 kg (58.4 kg/watershed ha). If the assumption of 100 kg N/ha for corn, 50 kg N/ha for hay and pasture and 30 kg N/ha for all small grains were applied, watershed application rates exceeded recommended rates in a number of watersheds. This

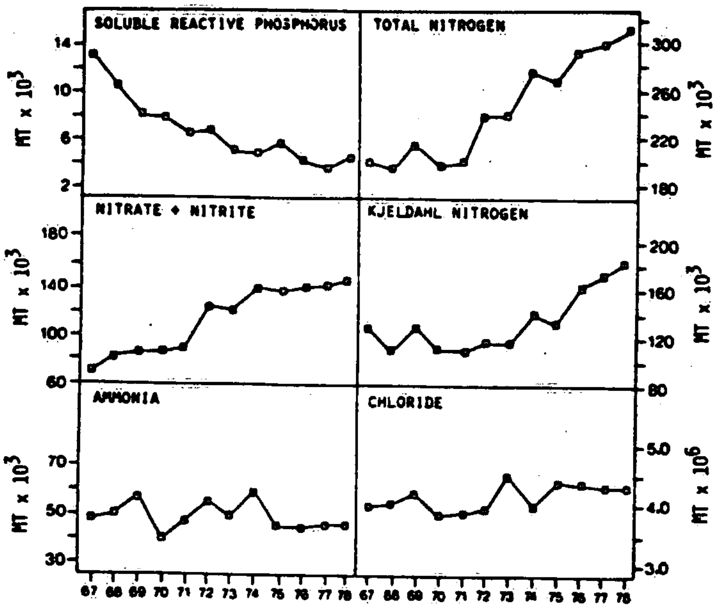


Fig. 6. Loadings of phosphorus,nitrogen and chloride to Lake Erie: 1967-1978 (from Lam et al, 1983)

situation probably reflected high N fertilizer rates on the large amounts of corn, vegetables, and tobacco found in these watersheds.From about 40-90% of N application in the surveyed watersheds was applied on corn. Corn area and tons of N fertilizer sold in Ontario showed 4- and 6-fold increases respectively from 1960 to 1976 (Fig.7).The future increased cultivation of corn could result in increased N loads especially to Lake Huron and Lake Ontario.

4. Atmospheric loading. Population densities and intensive agriculture can account for nitrate increases perhaps in the lower Great Lakes. Yet, as shown earlier, Lake Superior, where agricultural activities and population density are minimal, has experienced so far the most dramatic increase. The most obvious source of nitrates appears to be atmospheric precipitation, or acid rain.

During the past two decades, acid rain has often been cited as the major environmental problem facing eastern North America. Acid rain (including precipitation in the form of snow or fog and fall-out of dry particulate matter) is produced when sulphur dioxide (SO2) and nitrogen oxide (NOx) emissions are converted in the atmosphere to acidic compounds (sulphates and nitrates) and return to earth as precipitation or particulate matter. The effects of acid rain are often felt in areas far from the actual sources of emissions. The term `long-range transport of airborne pollutants', is used to describe this phenomenon. Major sources of nitrogen

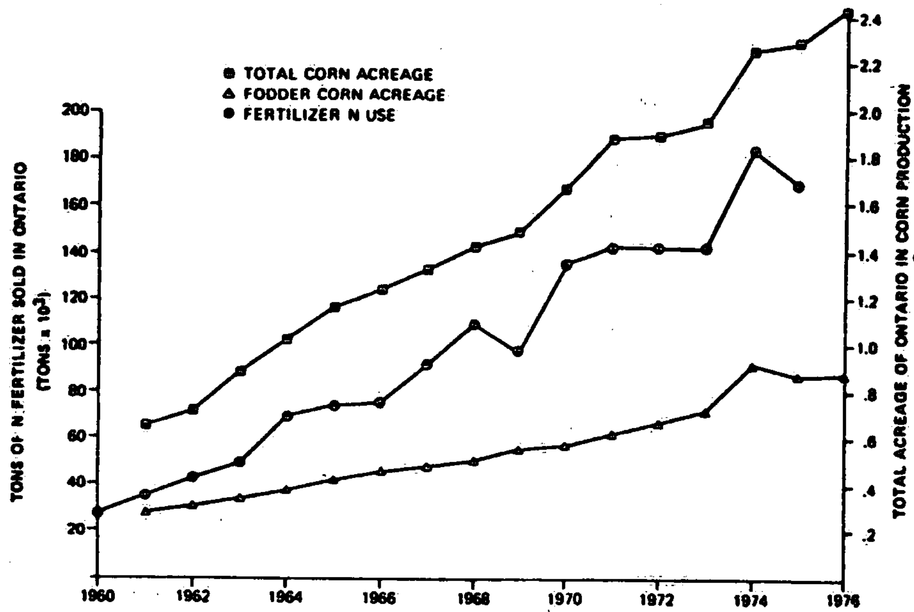


Fig. 7. Corn acreage and N fertilizer sales in Ontario, 1960-1976 (from Neilson et al, 1978)

oxides are automobile emissions, industrial processes, and power generating plants. Sulphur compounds can remain in the atmosphere for two to five days. Nitrogen compounds, on average remain in the upper atmosphere up to two days and are therefore found somewhat closer to emission sources (Bird and Rapport,1986).

Information on trends in the emission of SO2 and NOx in the most affected regions of the United States and Canada since 1955 is presented in Table 1. There was a substantial increase in NOx emissions, from 0.64 to 1.75 millions of tonnes per year between 1950-1980.

Table 1. Historical Trends in NOx Emissions (adapted from Bird and Rapport, 1986)

| | NOx millions of tonnes/year | | | |
|---|---|---|---|---|
| | U.S.A. | | Canada | |
| Year | Northeast & Midwest | Total | Eastern | Total |
| 1955 | 3.8 | 8.2 | 0.45 | 0.64 |
| 1965 | 5.5 | 13.1 | 0.56 | 0.85 |
| 1975 | 6.1 | 16.4 | 0.99 | 1.60 |
| 1980 | 5.5 | 19.3 | 1.05 | 1.75 |

Bennett (1986) attributed NO3 increases in Lake Superior almost entirely to an increasing rate of deposition from the atmosphere. Nitrogen oxides in the atmosphere are rapidly converted to nitric acid and organic nitrates and scrubbed out by precipitation. It follows that an increase of nitrogen emission to the atmosphere over the industrial heartland of North America will be accompanied by a similar increase in the amount of nitrogen deposited from the atmosphere into the Lake Superior basin. Chan and Perkins (1985) reported on 4-year data collection of rainwater samples on 3 stations in Lake Superior. The concentrations varied from 0.26 to 0.73 mg/l NO3-N and 0.19 to 0.40 mg/l NH4-N over the study period.Bennett estimated that nitrogen input to Lake Superior for 1973 totalled 95,200 tons, of which 56,000 tons (60 percent) was due to precipitation directly on the lake surface. Precipitation delivered 86,000 tons to the land area in the drainage basin of which 36,500 tons reached the lake via tributaries.

It can be concluded that the dramatic increases of nitrate in the Great Lakes are a result of several factors, which may assume different orders of importance: in the lower Great Lakes, the increased human population, increased use of fertilizers in agriculture and phosphorus reductions are predominant, whereas in the upper Great Lakes (Huron, Superior) it is primarily atmospheric deposition of nitrates from what is commonly termed "acid rain".

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REFERENCES

Allan,R.J.,and B.C.Kenney.1978.Rehabilitation of eutrophic prairie lakes in Canada.Verh.Internat.Verein.Limnol.20:214-224.

Bennett,E.B.1986.The nitrifying of Lake Superior.Ambio 15(5):272-275.

Bird,P.M.,and D.J.Rapport.1986.State of the Environment Report for Canada.Dept.of Environment,Ottawa.263 p.

Chan,C.H.,and L.H.Perkins.1985.Lake Superior wet deposition 1983.IWD-Water Quality Branch Internal Report,Burlington.17 p.

Dobson,H.F.H.1981.Trophic conditions and trends in the Laurentian Great Lakes.Water Quality Bulletin 6(4):146-151.

Forde,A.V.1979.A historical study of pollution of Burlington Bay.Reg.Mun.Ham.-Went.Ham.Munip.Lab.Report,Hamilton.57p.

Forsberg,C.1979.Die physiologischen Grundlagen der Gewasser - Eutrophierung.Wasser u.Abwasser Forschung,12,2:40-45.

Health and Welfare Canada.1978.Guidelines for Canadian Drinking Water Quality:Supporting Documentation.Ottawa.739 p.

International Joint Commission.1986.Third Biennial Report under the Great Lakes Water Quality Agreement of 1978 to the governments of the United States and Canada and the States and Provinces of the Great Lakes Basin.45 p.

Kwiatkowski,R.E.1984.Comparison of 1980 Lake Huron,Georgian Bay -North Channel Surveillance data with historical data.Hydrobiol.118:255-266.

Lam,D.C.L.,W.M.Schertzer,and A.S.Frazer.1983.Simulation of Lake Erie water quality responses to loadings and weather variations.IWD Scientific Series No.134.

Neilsen,G.H.,J.L.Culley,and D.R.Cameron.1978.Nitrogen loadings from agricultural activities in the Great Lakes Basin.Integration Report on Nitrogen.International Joint Commission,103 p.

Painter,D.S.,and G.Kamaitis.1985.Reduction of Cladophora biomass and tissue phosphorus in Lake Ontario,1972-1983.NWRI Contribution No.85-39,Burlington.13 p.

Robinson,G.W.1986.Water quality of the Bay of Quinte,Lake Ontario,before and after reductions in phosphorus loading.Can.Spec.Publ.Fish.Aquat.Sci.86:50-58.

Severn Sound Remedial Action Plan.1987.Ministry of the Environment,Ministry of Natural Resources and Environment Canada Report,Toronto,67 p.

Smith,V.H.1983.Low nitrogen to phosphorus ratios favor dominance by blue-green algae in lake phytoplankton.Science 221 (4611):669-671.

Stevens,R.J.J.,and M.A.T.Neilson.1987.Response of Lake Ontario to reductions to phosphorus load :1967-1982.Can.J.Fish.Aquat.Sci.44 (in press).

FIGURE CAPTIONS

Fig. 1. The Laurentian Great Lakes.

Fig. 2. Increases of springtime nitrate in the Great lakes,1960-1980 (from Dobson, 1981)

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